

The Action of Potassium Thiocyanate on the Chlorhydrins.

THESIS

SUBMITTED IN PARTIAL FULFILMENT OF THE REQUIRE-
MENTS FOR THE DEGREE OF DOCTOR OF PHILOS-
OPHY, IN THE FACULTY OF PURE SCIENCE,
COLUMBIA UNIVERSITY,

BY

WILBER DWIGHT ENGLE, A. M.

*Organic Laboratory, Havemeyer Hall,
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THE ACTION OF POTASSIUM THIOCYANATE ON THE CHLORHYDRINS.

I.

INTRODUCTION.

The first of the organic thiocyanates was prepared by A. Cahours in 1847. Several years earlier than that, as mentioned by Cahours in his announcement of the new compounds containing sulfur,¹ Liebig had described, under the name of "Schwefelcyanäthyl" a new compound which he obtained by the distillation of a mixture of alcohol, sulfuric acid, and potassium thiocyanate. This result was later questioned and many chemists of that time considered the possible existence of such compounds as very doubtful. The question was settled by the preparation, purification, and analysis of methyl and ethyl thiocyanates by Cahours. The method used was the distillation of equal parts of calcium methyl sulfate and potassium thiocyanate. The ethyl thiocyanate was prepared in a similar manner.

Since that time various investigators have prepared compounds containing the thiocyan group and have studied their behavior with different reagents. Of these thiocyanates, by far the greater number are the simple mono derivatives of the marsh-gas hydrocarbons. Only four di- and one trisubstitution products are known.

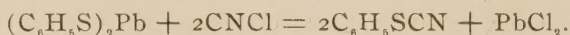
In addition to these thiocyanates of the simple hydrocarbons, a few have been prepared from some of the classes of derived compounds. Some of the important classes are entirely without representatives, while those that have their thiocyanates have only a very few that are known. The haloid ethers, the aldehydes, the ketones, the acids, the sulfonic acids, and the nitrils of the marsh-gas series have thiocyan derivatives. Among the aromatic compounds the

¹ Cahours : Ann. Chem (Liebig), 61, 95.

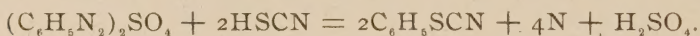
thiocyanates of some of the halogen, nitro, and amido compounds are known.

Several methods of preparation, aside from the original one of distillation of a mixture of calcium methyl sulfate and potassium thiocyanate in concentrated aqueous solution, have been used. Perhaps the best and most generally applicable is that of double decomposition between a haloid ether and a metallic thiocyanate, usually potassium, in alcoholic solution. In the preparation of the thiocyanaldehydes, Chautard found it necessary to use the iodoaldehyde and silver thiocyanate in ether solution.

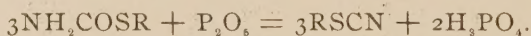
The treatment of lead mercaptid with chlorcyan is useful in some cases :¹



Phenyl thiocyanate is also obtained by the action of thiocyanic acid on diazobenzene sulfate :²



The action of phosphorus pentoxid on monothiocarbamates also gives thiocyanates :

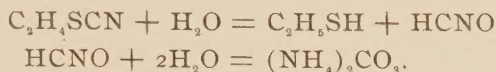


One property, at least, the liquid thiocyanates seem to have in common, that of a very disagreeable, garlic odor. Most of them produce a burning or smarting sensation on the skin, somewhat as their isomers, the mustard oils, do although much less intense. The methylene, ethylene, and trimethylene dithiocyanates and allyl trithiocyanate are crystallizable solids. Other thiocyanates of the marsh-gas series are liquids. The phenyl orthobromobenzyl and benzoyl thiocyanates and the phenylthiocyanacetone among the aromatic compounds are liquids and other compounds containing the group are solids. As a class they are insoluble, or very nearly so, in water, readily soluble in alcohol, ether, chloroform, and most of the organic solvents. In general they give the following reactions with the ordinary reagents :

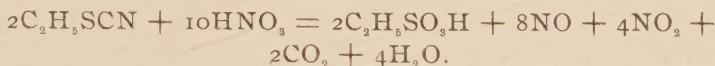
¹ Henry : Ber. d. chem. Ges., **2**, 637.

² Billeter : Ber. d. chem. Ges., **7**, 1753.

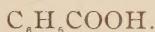
1. Water at 200° , with a trace of sulfuric or hydrochloric acid, gives mercaptan and ammonium carbonate :¹



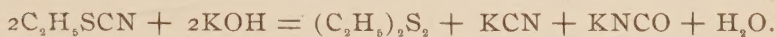
2. Nitric acid, at 100° , gives sulfonic acid of the same radical :²



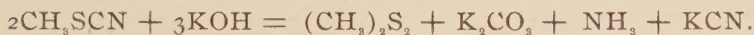
Benzyl thiocyanate, however, is oxidized to benzoic acid :



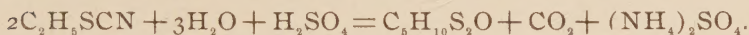
3. Strong aqueous potassium hydroxid gives a disulfid of the radical and potassium cyanid and cyanate :³



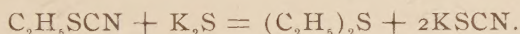
4. Alcoholic potassium hydroxid yields the disulfid of the radical and potassium carbonate :⁴



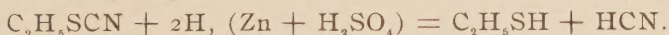
5. Strong sulfuric acid gives di-thiocarbonic esters :⁵



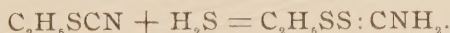
6. Potassium sulfid yields a sulfid of the radical and potassium thiocyanate :⁶



7. Nascent hydrogen reduces a thiocyanate to the mercaptan :⁷



8. Hydrosulfuric acid (dry) gives dithiocarbamic ester :⁸



Some tables, showing the different known thiocyanates, giving the formula, melting- or boiling-point, by whom first pre-

¹ Hofmann : Ber. d. chem. Ges., **1**, 180.

² Cahours : Ann. chim. phys., [3], **18**, 262.

³ Bruning : Ann. Chem. (Liebig), **104**, 190.

⁴ Löwig : Pogg. Ann., **67**, 101.

⁵ Schmitt and Glutz : Ber. d. chem. Ges., **1**, 166.

⁶ Löwig : Pogg. Ann., **67**, 102.

⁷ Hofmann : Ber. d. chem. Ges., **1**, 177.

⁸ James : J. prakt. Chem., [2], **30**, 316.

pared and how, have been made and are here reproduced. Table I contains the thiocyanates of the simple hydrocarbons of the marsh-gas and aromatic series. One class of compounds, the sulfin cyanids, while containing the group SCN, are not included, as they are cyanids of the radical R_3S rather than thiocyanates.

Table II contains the thiocyanates of the haloid ethers, the sulfonic acids, the nitrils, and nitro and amido compounds of both aromatic and marsh-gas series.

Table III contains the known thiocyan acids, their esters and other derivatives.

Table IV contains the acid thiocyanates or the thiocyanates of the acid radicals.

Table V contains the known thiocyan aldehydes and ketones.

TABLE I.
THIOCYANATES OF THE HYDROCARBONS.

Name.	Formula	Melting-point	Boiling-point.	Preparation and reference
Methyl thiocyanate...	CH_3SCN		133°	$\text{Ca}(\text{CH}_3\text{SO}_4)_2 + \text{KSCN}$. Cahours : A., 61, 95. $(\text{CH}_3\text{S})_2\text{Pb} + \text{CNBr}$. Cahours : J., 1875, 257.
Methylene dithiocyanate.....	$\text{CH}_2(\text{SCN})_2$	102		$\text{CH}_2\text{I}_2 + \text{KSCN}$. Lermontow : B., 7, 1282.
Methyl thiocyanate.....	$(\text{CH}_3)_4(\text{SCN})_3$			CH_3SCN heated to 180°. Hofmann : B., 13, 1349.
Ethyl thiocyanate.....	$\text{C}_2\text{H}_5\text{SCN}$		146	$\text{Ca}(\text{C}_2\text{H}_5\text{SO}_4)_2 + \text{KSCN}$. Cahours : A., 61, 95.
Ethylene dithiocyanate.....	$\text{C}_2\text{H}_4(\text{SCN})_2$	90		$\text{CH}_2\text{ClCH}_2\text{Cl} + \text{KSCN}$. Sonnenschein : J., 1855, 609.
Propyl thiocyanate.....	$\text{C}_3\text{H}_7\text{SCN}$		163	$\text{CH}_3\text{BrCH}_2\text{Br} + \text{KSCN}$. Glutz : A., 153, 313. Schmidt : Z., 1870, 576.
Isopropyl thiocyanate.....	$\text{CH}_3\text{CHSCNCH}_3$		152-3	Henry : B., 2, 496.
Propylene dithiocyanate.....	$\text{CH}_2\text{SCNCHSCNCH}_3$	oil		$\text{CH}_2\text{BrCHBrCH}_3 + \text{KSCN}$. Hagelburg : B., 23, 1085.
Trimethylene dithiocyanate.....	$\text{CH}_2\text{SCNCH}_2\text{CH}_2\text{SCN}$	23		$\text{CH}_2\text{BrCH}_2\text{CH}_2\text{CH}_2\text{Br} + \text{KSCN}$. Hagelburg : B., 23, 1083.
Allyl thiocyanate.....	$\text{C}_3\text{H}_5\text{SCN}$	Decomp	Decomp	$(\text{C}_3\text{H}_5)_3\text{Pb} + \text{CNCl}$. Billeter : B., 8, 464.
Allyl trithiocyanate.....	$\text{C}_3\text{H}_5(\text{SCN})_3$	126		$\text{C}_3\text{H}_5\text{Br} + \text{NH}_4\text{SCN}$. Gerlicke : A., 178, 85.
Propargyl thiocyanate.....	$\text{C}_4\text{H}_5\text{SCN}$			$\text{C}_3\text{H}_5\text{Br}_3 + \text{KSCN}$. Henry : B., 2, 637.
Isobutyl thiocyanate.....	$(\text{CH}_3)_2\text{CHCH}_2\text{SCN}$		Decomp 174-6	$\text{C}_4\text{H}_9\text{Br} + \text{KSCN}$. Henry : B., 6, 729. $\text{Ca}(\text{C}_4\text{H}_9\text{SO}_4)_2 + \text{KSCN}$. Reimer : B., 3, 757.

TABLE I. (*Continued.*)

THIOCYANATES AND THE HYDROCARBONS.

Name.	Formula.	Melting- point.	Boiling- point.	Preparation and reference.
Isoamyl thiocyanate.	$(\text{CH}_3)_2\text{CH}_2\text{CH}_2\text{CH}_2\text{SCN}$		197	Medlock: B., 69, 222.
Hexyl thiocyanate...	$\text{C}_6\text{H}_{13}\text{SCN}$		215-20	Cahours and Pelouse: J., 1863, 526.
2d Hexyl thiocyanate	$\text{C}_4\text{H}_9\text{CHSCNCH}_3$		206	Uppenkamp: B., 8, 55.
Heptyl thiocyanate...	$\text{C}_7\text{H}_{15}\text{SCN}$		235-6	$\text{C}_2\text{H}_5\text{Br} + \text{KSCN}$. Bogert.
2d Octyl thiocyanate	$\text{C}_8\text{H}_{17}\text{SCN}$		142	$\text{C}_2\text{H}_5\text{Br} + \text{KSCN}$. Jahm: B., 8, 805.
Phenyl thiocyanate...	$\text{C}_6\text{H}_5\text{SCN}$		231	$(\text{C}_6\text{H}_5\text{S})_2\text{Pb} + \text{CNCl}$. Henry: B., 2, 637.
Benzyl thiocyanate...	$\text{C}_6\text{H}_5\text{CH}_2\text{SCN}$	41		$(\text{C}_6\text{H}_5\text{N})_2\text{SO}_4 + \text{HSCN}$. Billeter: B., 7, 1753.
2-6 Naphthalene di-thiocyanate	$\text{C}_{10}\text{H}_6(\text{SCN})_2$	91		$\text{C}_6\text{H}_5\text{CH}_2\text{Br} + \text{KSCN}$. $(\text{C}_{10}\text{H}_6\text{S}_2)_2\text{Pb}_2 + \text{CNCl}$. Bram: B., 25, 2738.

TABLE II.
SUBSTITUTED THIOCYANATES.

Name.	Formula.	Melting-point.	Boiling-point.	Preparation and reference.
Chlorethyl thiocyanate.....	$\text{CH}_2\text{ClCH}_2\text{SCN}$	below -20	202	$\text{CH}_2\text{ClCH}_2\text{Br} + \text{KSCN}$. James : J. pr., [2] 20, 352.
Chlorallyl thiocyanate.....	$\text{CH}_2 : \text{CClCH}_2\text{SCN}$			$\text{CH} : \text{CClCH}_2\text{Cl} + \text{KSCN}$. Henry : B., 39, 526.
Orthobrombenzyl thiocyanate.....	$\text{C}_6\text{H}_4\text{BrCH}_2\text{SCN}$	oil		$\text{C}_6\text{H}_4\text{BrCH}_2\text{Br} + \text{KSCN}$.
Parabrombenzyl thiocyanate.....	$\text{C}_6\text{H}_4\text{BrCH}_2\text{SCN}$	25		$\text{C}_6\text{H}_4\text{BrCH}_2\text{Br} + \text{KSCN}$. Jackson and Lowery : B., 10, 1209.
Parachlorbenzyl thiocyanate.....	$\text{C}_6\text{H}_4\text{ClCH}_2\text{SCN}$	17		$\text{C}_6\text{H}_4\text{ClCH}_2\text{Br} + \text{KSCN}$. Jackson and Field : Am., 2, 91.
Iodobenzyl thiocyanate.....	$\text{C}_6\text{H}_4\text{ICH}_2\text{SCN}$	40		
Butyric nitril thiocyanate.....	$\text{CH}_3\text{SCNCH}_2\text{CH}_2\text{CN}$		195	$\text{CH}_2\text{ClCH}_2\text{CH}_2\text{CN} + \text{KSCN}$. Gabriel : B., 23, 2490.
Toluic nitril thiocyanate.....	$\text{C}_6\text{H}_4\text{CNCH}_2\text{SCN}$	86		$\text{C}_6\text{H}_4\text{CNCH}_2\text{Cl} + \text{KSCN}$. Gabriel : B., 23, 2490.
Orthonitrobenzyl thiocyanate.....	$\text{C}_6\text{H}_4\text{NO}_2\text{CH}_2\text{SCN}$	75		$\text{C}_6\text{H}_4\text{NO}_2\text{CH}_2\text{Cl} + \text{KSCN}$. Cassirer : B., 25, 3028.
Paranitrobenzyl thiocyanate.....	$\text{C}_6\text{H}_4\text{NO}_2\text{CH}_2\text{SCN}$	needles		$\text{C}_6\text{H}_4\text{NO}_2\text{CH}_2\text{Cl} + \text{KSCN}$. Henry : B., 2, 658.
1 : 2 : 4 Dinitrophenyl thiocyanate.....	$\text{C}_6\text{H}_3(\text{NO}_2)_3\text{SCN}$	139		$\text{C}_6\text{H}_3(\text{NO}_2)_3\text{Br} + \text{KSCN}$. Austin and Smith : Am., 8, 89.
Orthoamidobenzyl thiocyanate.....	$\text{C}_6\text{H}_4\text{NH}_2\text{CH}_2\text{SCN}$	137-8		$\text{C}_6\text{H}_4\text{NO}_2\text{CH}_2\text{SCN} + \text{SnCl}_2 + \text{HCl}$. Cassirer : B., 25, 3029.
β -Thiocyanethyl phthalimid.....	$\text{C}_8\text{H}_4\text{O}_2 : \text{NCH}_2\text{CH}_2\text{SCN}$	108		$\text{C}_8\text{H}_4\text{O}_2 : \text{NCH}_2\text{CH}_2\text{Cl} + \text{KSCN}$. Coblenitz : B., 24, 2131.

TABLE II. (*Continued.*)
SUBSTITUTED THIOCYANATES.

Name.	Formula.	Melting-point.	Boiling-point.	Preparation and reference.
β -Thiocyanopropyl phthalimid	$C_8H_4O_2 : NCH_2CHSCNCH_3$	89-93		$C_8H_4O_2 : NCH_2CHBrCH_3 + KSCN$. Gabriel and Lauer : B., 23, 89.
γ -Thiocyanopropyl phthalimid	$C_8H_4O_2 : NCH_2CH_2CH_2SCN$	96-98		$C_8H_4O_2 : NCH_2CH_2CH_2Br + KSCN$. Gabriel and Lauer : B., 23, 89.
Thiocyanethyl sulfonic acid	$CH_2SCNCH_2SO_3H$			$CH_2SCNCH_2Cl + Na_2SO_3$. James : J. pr., [2] 26, 381.

TABLE III.
THIOCYAN ACIDS AND DERIVATIVES.

Name.	Formula.	Melting-point.	Boiling-point.	Preparation and reference.
Thiocyanformic ethyl ester.....	$\text{SCNCOOC}_2\text{H}_5 + \text{C}_2\text{H}_5\text{OH}$	43-44		$\text{ClCOOC}_2\text{H}_5 + \text{NH}_4\text{SCN}$. Delitsch : J. pr., [2] 10, 108.
Thiocyanacetic acid.	$\text{CH}_2\text{SCNCOOH}$		Decomp	$\text{CH}_2\text{ClCOONa} + \text{KSCN}$. Claeson : B., 10, 1347.
Thiocyanacetic ethyl ester.....	$\text{CH}_2\text{SCNCOOC}_2\text{H}_5$		225	$\text{CH}_2\text{ClCOOC}_2\text{H}_5 + \text{KSCN}$. Heintz : A., 136, 223.
Thiocyan acetic isomyl ester.....	$\text{CH}_2\text{SCNCOOC}_5\text{H}_{11}$		Decomp	
Thiocyan acetamid	$\text{CH}_2\text{SCNCONH}_2$			
Polymerid, thiocyan acetic acid.....	$(\text{CH}_2\text{SCNCOOH})_3$	200		$\text{CH}_2\text{ClCOOK} + \text{K}_2(\text{SCN})_3$. Claeson : J. pr., [2] 33, 127.
Perthiocyan diacetic acid.....	$\text{C}_2\text{N}_2\text{S}(\text{SCH}_2\text{COOH})_2$	177		$\text{CH}_2\text{ClCOONa} + \text{H}_2\text{C}_2\text{N}_2\text{S}_3$. Klason : J. pr., [2] 38, 391.
Rhodanic acid.....	$\text{CH}_2\text{SCNCONHSC:S}$	168-70		$\text{CH}_2\text{ClCOOH} + \text{NH}_4\text{SCN}$. Nencki : J. pr., [2] 16, 1.
Ethylidene rhodanic acid.....	$\text{CH}_3\text{CH:CSHCOSCN}$	147		$\text{C}_2\text{H}_5\text{ONH}_3 + \text{C}_3\text{H}_3\text{NS}_2\text{O}$. Nencki : B., 17, 2278.
Benzylidene rhodanic acid.....	$\text{C}_6\text{H}_5\text{CH:CSHCOSCN}$	200		$\text{C}_6\text{H}_5\text{CHO} + \text{C}_3\text{H}_3\text{NS}_2\text{O}$. Nencki : B., 17, 2278.
Thiocyanbarbituric acid	$\text{CO} \begin{matrix} \text{NHCO} \\ \text{CHSCN} \end{matrix} \text{NHCO}$			Trzeinski : B., 16, 1058.
Thiocyanamino cinamic acid	$\text{C}_6\text{H}_4\text{NH}_3\text{SCNCH}_2\text{CH}_2\text{COOH}$			$\text{C}_6\text{H}_4\text{NH}_3\text{ClCH}_2\text{CH}_2\text{COOH} + \text{KSCN}$. Rothschild : B., 23, 3342.

TABLE IV.
ACID THIOCYANATES.

Name.	Formula.	Melting-point.	Boiling-point.	Preparation and reference.
Acetyl thiocyanate ..	CH_3COSCN		132-133	$\text{CH}_3\text{COCl} \cdot \text{Pb}(\text{SCN})_2$. Miquel : A. ch., [5] 11,
Butyryl thiocyanate.	$\text{C}_3\text{H}_7\text{COSCN}$		180	$\text{C}_3\text{H}_7\text{COCl} + \text{Pb}(\text{SCN})_2$. Miquel : A. ch., [5] 11,
Benzoyl thiocyanate	$\text{C}_6\text{H}_5\text{COSCN}$		Liquid	$\text{C}_6\text{H}_5\text{COCl} + \text{Pb}(\text{SCN})_2$. Miquel : A. ch., [5] 11,

TABLE V.
ALDEHYDES AND KETONES.

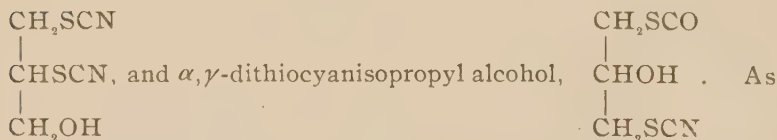
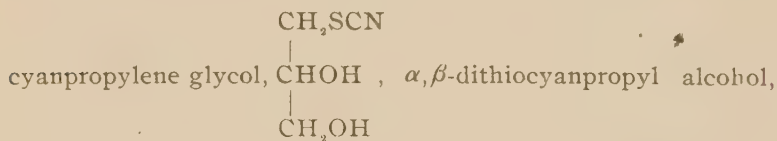
Name.	Formula.	Melting-point.	Boiling-point.	Preparation and reference.
Thiocyan ethyl aldehyde.....	$\text{CH}_2\text{SCN}.\text{CHO}$	Below -20	Decomp	$\text{CH}_2\text{I}.\text{CHO} \rightarrow \text{AgSCN}$. Chautard : A. d. ch., [6] 16, 193.
3-Thiocyanpropyl aldehyde.....	$\text{CH}_2\text{SCNCH}_2\text{CHO}$		Decomp	$\text{CH}_2\text{I}.\text{CH}_2\text{CHO} + \text{AgSCN}$. Chautard : A. d. ch., [6] 16, 197.
α -thiocyanisobutyric aldehyde.....	$(\text{CH}_3)_2\text{C}.\text{SCN}.\text{CHO}$		Decomp	$(\text{CH}_3)_2\text{CI}.\text{CHO} + \text{AgSCN}$. Chautard : A. d. ch., [6] 16, 197.
Thiocyanisovaleric aldehyde.....	$(\text{CH}_3)_2\text{CSCNCH}_2\text{CHO}$		Decomp	$(\text{CH}_3)_2\text{CI}.\text{CH}_2\text{CHO} + \text{AgSCN}$. Chautard : A. d. ch., [6] 16, 198.
Thiocyanheptoi aldehyde.....	$\text{CH}_2\text{SCN}(\text{CH}_2)_5\text{CHO}$		Decomp	$\text{CH}_2\text{I}(\text{CH}_2)_5\text{CHO} \rightarrow \text{AgSCN}$. Chautard : A., d. ch. [6] 16, 108.
Thiocyanacetone	$\text{CH}_3\text{SCN}.\text{CO}.\text{CH}_3$	135		$\text{CH}_2\text{Cl}.\text{COCH}_3 + \text{Ba}(\text{SCN})_2$. Tschnerniac : B., 16, 349. Arapides : A., 249, 18.
Thiocyanoxim.....	$\text{CH}_2\text{SCN}.\text{CNOHCH}_3$	80		$\text{C}_4\text{H}_7\text{SCOCH}_2\text{Br} + \text{KSCN}$. Brunswick : B., 19, 2893.
Thiocyanmethylthi-enyl ketone.....	$\text{C}_4\text{H}_7\text{SCOCH}_2\text{SCN}$	74		$\text{C}_6\text{H}_5\text{COCH}_2\text{Br} + \text{Ba}(\text{SCN})_2$. Arapides : A., 249, 10.
Phenyl thiocyan-methylketone	$\text{C}_6\text{H}_5.\text{COCH}_2\text{SCN}$	L	Liquid	$\text{C}_6\text{H}_5\text{COC}_2\text{H}_4\text{Br} \rightarrow \text{KSCN}$. Pampel : B., 19, 2897.
Phenylthiocyan-ethyl ketone	$\text{C}_6\text{H}_5\text{COC}_2\text{H}_4\text{SCN}$			

II.

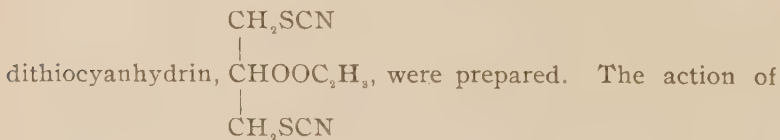
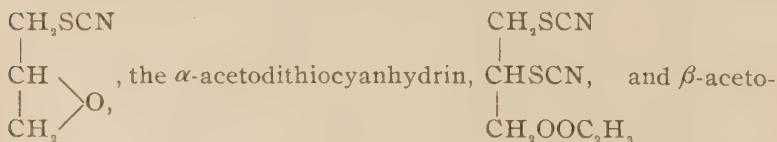
EXPERIMENTAL, PART.

The alcohols form the most important class of organic compounds which have no representatives containing the thiocyan group. It would seem that such compounds would be produced by the double decomposition between alcohols having one or more atoms of hydrogen displaced by halogen and a metallic thiocyanate, and it was with this expectation that the following experiments were undertaken. In all cases tried, a reaction occurred as was shown by the separation of the halogen salt. The thiocyanates formed, however, seem to be very unstable, easily changing to resinous substances, and much difficulty was experienced in separating and purifying them. In some cases it was found impossible.

The particular thiocyan alcohols, whose preparation was undertaken, are those derived from propane; namely, α -thio-



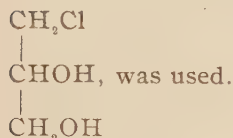
being of a somewhat similar nature, the epithiocyanhydrin,



potassium thiocyanate on chloranil was also tried.

α-thiocyanhydrin.

For the attempted preparation of *α*-thiocyanpropylene glycol, the corresponding *α*-chlorpropylene glycol or monochlorhydrin,



A mixture of 14 grams of monochlorhydrin and 13 grams of potassium thiocyanate, with 95 per cent. alcohol for solution, were heated on the water-bath with a return condenser. A crystalline precipitate of potassium chlorid gradually formed. After four days of heating, 4 grams of potassium chlorid in place of 10 grams, theoretical quantity, had separated. The filtrate from the potassium chlorid was again heated. Only a little more of the chlorid separated but there formed a considerable amount of a white resinous substance, some of which was removed from the flask and examined. Washed with hot water and alcohol it is a white or light yellow, brittle, odorless substance. It is insoluble in ordinary organic solvents, including water, alcohol, ether, benzene, benzine, chloroform, carbon disulfid, kerosene, gasolene and toluene. It is unaffected by hydrochloric, acetic and sulfuric acids or by ammonium hydroxid or strong aqueous potassium hydroxid. Bromine decomposes it with the production of a tar-like substance. Strong nitric acid oxidizes it, producing sulfuric and oxalic acids. This is an interesting reaction since it shows that the sulfur is much less closely bound to the radical than in the case of thiocyanates, mercaptans and sulfids which, by oxidation with nitric acid, yield sulfonic acid, sulfoxyds and similar compounds.

That this resinous substance is not a thiocyanate is shown by the following facts: It does not give a sulfid with potassium hydroxid. It does not give a mercaptan with zinc and sulfuric acid. It does not give a sulfid and potassium thiocyanate with potassium sulfid. It does not give a sulfonic acid by the oxidation with nitric acid. Its solubilities are not those of known thiocyanates.

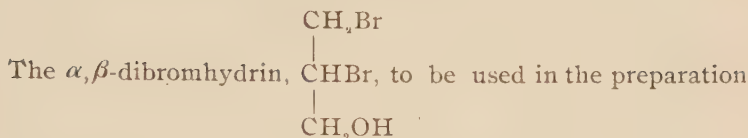
An analysis of the substance carefully washed with water and alcohol and dried to a constant weight, gave the following percentages.

	I.	II.	III.	IV.	V.	Average.
Carbon	40.127	40.163				40.145
Hydrogen	5.185	5.15				5.168
Nitrogen			7.531	7.590		7.560
Sulfur					27.281	27.281
Oxygen						19.846

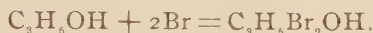
These percentages indicate that a secondary reaction has produced a complex condensation product. The absence of any solvent prevented any attempt to crystallize this compound. A flask, containing a mixture of potassium thiocyanate and monochlorhydrin, after heating was set aside. After several weeks it was examined and well formed crystals were found. The properties of these crystals were identical with those of the substance just described.

Besides the insoluble white substance there was also found, in the alcoholic filtrate from the potassium thiocyanate and monochlorhydrin, a very small amount of oil having the garlic odor characteristic of the organic thiocyanates. This oily liquid is extremely unstable. Any attempt to purify it changes it to the insoluble white substance. Apparently monothiocyanate is first formed by the reaction, and by some secondary condensation the insoluble compound results.

The reaction between potassium thiocyanate and monochlorhydrin was also tried at higher temperatures. Sealed tubes containing these two compounds in the ratio of their molecular weights, with alcohol as a solvent, were heated to different temperatures. Below 100° the action was very slow. From 110° to 115°, the reaction was complete in six hours. At 120° and above there was much decomposition. In all cases the products are the same: the insoluble white compound and a trace of what was considered the monothiocyanhydrin. It was impossible to secure this in amount sufficient for further study.

The α,β -dithiocyanhydrin.

of α,β -dithiocyanhydrin, was obtained by the direct addition of bromine to allyl alcohol.

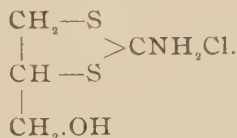


The product was purified by distillation *in vacuo*.

An alcoholic solution of 40 grams of this dibromhydrin and 37 grams of potassium thiocyanate, were heated on the water-bath for six days. Somewhat more than half the theoretical quantity of potassium bromid separated. As there were signs of decomposition the heating was stopped. By evaporation of the alcohol, washing with water, and collecting with ether, about 10 cc. of dark-colored liquid was obtained. Heated with potassium sulfid solution it gave potassium thiocyanate easily identified by the ferric chloride test. On heating or attempting to distil with steam it was resinified.

The reaction was next tried in sealed tubes. The tubes were charged with potassium thiocyanate and dibromhydrin, in the ratio of two molecules of the former to one of the latter. Alcohol was added as a solvent. Between 110° and 115° the reaction was complete in about eight hours. At higher temperatures there was much decomposition. In all cases there was a tendency to produce an amorphous substance similar to that from the monohydrin. The contents of the tubes were treated with warm alcohol. The alcoholic solution filtered from the potassium bromid was slowly evaporated to a small bulk and carefully washed with water to remove any unchanged potassium thiocyanate. There was left an oily liquid which could be further purified by solution in ether. This treatment does not remove all the unchanged dibromhydrin. The compound decomposes on heating, hence can not be distilled. The difficulty of securing a pure sample prevented analysis. That the liquid is dithiocy-

anhydrin is shown by the fact that it gives potassium thiocyanate on heating with potassium sulfid and the yield of potassium bromid is nearly equal to the theoretical. Additional proof is found in the preparation from it of iminomethanepropylalcohol-disulfid hydrochlorid of the formula

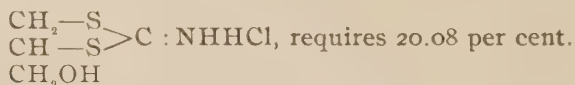


A similar reaction is found in the case of methylene dithiocyanate and propylene dithiocyanate. Both compounds have adjacent thiocyan groups as in the case of the compound under discussion and both give imino compounds similar to that above.¹

About 10 cc. of dithiocyanhydrin was poured in 50 cc. of water and a few grams of granulated tin added. The mixture was carefully heated on the water-bath and hydrochloric acid added. In the course of an hour's boiling the oily dithiocyanhydrin disappeared. Upon evaporation to a small bulk crystals appeared. When the liquid was left to spontaneous evaporation large octahedrons were obtained of iminomethanepropylalcohol-disulfid tin hydrochlorid.

The compound is not stable in solution as the tin (stannous) is oxidized at the expense of the rest of the compound producing stannic chlorid and a resinous substance. It was found advisable to precipitate the tin immediately after the dithiocyanhydrin had gone into solution, with hydrosulfuric acid leaving the hydrochloric salt of iminomethanepropylalcohol-disulfid in solution. The solution, filtered from the tin sulfid, was evaporated to dryness on the water-bath.

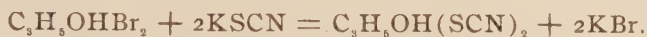
The residue was dissolved in alcohol, filtered, evaporated to a small bulk, and allowed to crystallize. Transparent, colorless, well-formed, tetragonal crystals separated. A determination of the chlorine gave 20.21 per cent. while the formula



¹ Hagelberg : Ber. d. chem. Ges., 23, 1083.

This iminomethanepropylalcoholdisulfid hydrochlorid is very easily soluble in water, somewhat soluble in alcohol, and insoluble in ether and chloroform.

The preparation of this compound taken with the reactions with potassium sulfid and the amount of potassium bromid separated, identify the dithiocyanhydrin. The reaction for its preparation is



In its physical properties it closely resembles the propylene-dithiocyanate. Both are liquids of garlic-like odor, insoluble in water, but soluble in alcohol and ether. Both are decomposed by heat and resinified by acids and alkalies. By nitric acid both are oxidized, producing sulfuric acid and, in the case of dithiocyanhydrin, oxalic acid is also formed. The action of the nitric acid seems to be to first produce a substance similar to the amorphous compound from the monochlorhydrin which is then oxidized as above.

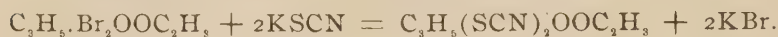
α-Acetodithiocyanhydrin.

Acetodibromhydrin, or dibrompropyl acetate, is prepared by the action of acetic anhydrid on the α,β -dibrompropyl alcohol.¹ It was washed with water and a dilute carbonate solution dried and rectified under diminished pressure.

A sealed tube containing 1 gram of acetodibromhydrin, 13 grams of potassium thiocyanate, and 10 cc. of alcohol, was kept at 120° for four hours. On opening, nearly the theoretical quantity of potassium bromid was found. The alcoholic filtrate from the potassium bromid was poured into water and about 15 cc. of a heavy liquid, insoluble in the water, separated. This was washed several times with water to free it from traces of potassium bromid and thiocyanate. It was then dissolved in ether to free it from decomposition-products. On evaporation there was left a clear, red-colored liquid, giving, with potassium sulfid, potassium thiocyanate. This compound, like the corresponding alcohol, cannot be distilled and is easily decomposed by most reagents. With tin and hydrochloric acid it gave reactions similar to those with the alcohol.

¹ Aschan: Ber. d. chem. Ges., **23**, 1827.

The compound was not analyzed but the reactions show it to be acetodithiocyanhydrin. The reaction is:



α,γ -Dithiocyanhydrin.

The dichlorisopropyl alcohol or dichlorhydrin was prepared by treating anhydrous glycerin with chlorid of sulfur at 100° . The product was fractionally distilled and the fraction collected between 176° and 178° , was used in these experiments.

A mixture of 12.5 grams of the dichlorhydrin and 19 grams of potassium thiocyanate in alcoholic solution was heated on the water-bath for four days. About 6 grams of potassium chlorid had separated, less than half the theoretical amount. The contents of the flask had the odor of the thiocyanates. In addition to the potassium chlorid, there had also separated a spongy mass, of a yellow color and in appearance not unlike the insoluble compound obtained from the monochlorhydrin. On examination it showed the same properties. It was insoluble in the organic solvents. It was unaffected by acids or alkalies. Reducing agents do not change it; strong nitric acid oxidizes it to sulfuric and oxalic acids. It is apparently a condensation-product similar to that obtained in case of monochlorhydrin.

In the alcoholic filtrate from the above compound was found a very small amount of a liquid, insoluble in water, having the characteristic odor of the thiocyanates. It may have been either the dithiocyanhydrin sought or the chlorthiocyanhydrin. Its insolubility in water would distinguish it from the dichlorhydrin. It was unstable and attempts to purify it sufficiently to test resulted in its decomposition.

This reaction was also tried in sealed tubes. A tube, heated to 130° for six hours, contained much unchanged potassium thiocyanate. Considerable of the spongy substance was found and a trace of the oily compound mentioned above. A tube heated to 175° for two hours gave the best results. The action was nearly complete. Less of the amorphous substance was formed. At higher temperatures there was much decomposition and pressure produced. In all cases the same results were

obtained. I was unable to separate and purify a compound containing the thiocyan group.

β-Aceto-α,γ-dithiocyanhydrin.

The corresponding acetic ester was also tried; that is, the dichlorisopropylacetate. The ester was prepared according to the method of Berthelot and Luca.¹ Anhydrous glycerin was treated with acetyl chlorid and the product purified by fractional distillation.

A sealed tube containing dichlorpropyl acetate and potassium thiocyanate in the ratio of one molecule of the former to two of the latter, with alcohol for solution, was heated to 130° for six hours. The action was incomplete and the tube was heated to 180°. There was some decomposition. A large amount of amorphous substance resembling those already described was present. A small amount of oil was also found as in the case of the corresponding alcohol. Here again apparently the thiocyanate is formed but suffers secondary decomposition resulting in the insoluble amorphous substance.

Epithiocyanhydrin.

Epithiocyanhydrin proved much easier in preparation and more interesting in reactions. For its preparation both epichlor-

hydrin, $\begin{array}{c} \text{CH}_2\text{Cl} \\ | \\ \text{CH} \\ | \\ \text{CH}_2 \end{array} > \text{O}$, and epibromhydrin were used. Epichlorhydrin

was obtained by the action of a strong aqueous solution of potassium hydroxid on dichlorisopropyl alcohol. The epibromhydrin was obtained in a similar manner from α,β-dibrompropyl alcohol. Both compounds were purified by distillation. Both react readily with potassium thiocyanate to form the epithiocyanhydrin.

There is no reaction between epibrom- or epichlorhydrins and potassium thiocyanates at ordinary temperatures. Mixtures of these substances have stood for several days without reaction.

¹ Ann. chim. phys., [3], 52, 459.

At 40° to 50°, however, the action goes on nicely. The theoretical amount of potassium halogen salt is separated in a few hours. At higher temperatures the action is violent; at 100° it is very rapid and there is much decomposition. The purification of the epithiocyanate is somewhat difficult as heat decomposes it. The alcoholic solution, filtered from the separated potassium chlorid or bromid, is evaporated to a small bulk, keeping the temperature below 50°. Water is then added to wash out the excess of potassium thiocyanate. A thick insoluble liquid separates; this is, the epithiocyanhydrin holding in solution much decomposition matter. It can be freed from this, after washing with water, by solution in ether.

The evaporation of the ether leaves the epithiocyanhydrin as a clear liquid of a dark red color, and having a disagreeable garlic odor. It is insoluble in water but soluble in alcohol, ether, and chloroform. It cannot be distilled. On the skin it produces a burning or smarting sensation. With potassium sulfid it gives potassium thiocyanate. With nitric acid it behaves like the compounds already described: the acid first resinifies and then oxidizes to sulfuric and oxalic acids.

A determination of the nitrogen confirms the qualitative results:

	Per cent.
Nitrogen found.....	11.914
Necessary for formula,	
CH ₂ SCN	
CH	
CH ₂ >O.....	12.17

The reaction is:



Action of Hydrosulfuric Acid on Epithiocyanhydrin.

Dry hydrosulfuric acid has an interesting reaction on the thiocyanates of the marsh-gas series. It forms the esters of dithiocarbamic acid which are readily crystallizable. About 10 cc. of epithiocyanhydrin was treated with hydrogen sulfid under a pressure of one atmosphere and 8 inches of mercury. The

experiment was tried both at ordinary temperatures and at 100°. In both cases the result was the same. No carbamic ester was formed but thick sirupy liquid of very disagreeable odor, insoluble in water and sparingly soluble in alcohol, carbon disulfid, and chloroform. Its alcoholic solution was precipitated by soluble lead, mercury, silver, and copper salts, but was unaffected by mercuric or lead oxids. These reactions indicate the formation of a sulfid.

Epithiocyandimethylsulfur Iodid.

A reaction similar to that used by Cahours in the preparation of trimethylsulfur iodid was tried. About 5 cc. of epithiocyanhydrin with 15 cc. of methyl iodid (an excess) were sealed in a tube and kept at 100° for six hours. On examination crystals were found in the tube. A similar mixture was allowed to stand for several days at the ordinary temperature and crystals also separated in this case. The crystals were clear, colorless, monoclinic plates. They were purified by recrystallizing from water, and washing with alcohol. They gave good qualitative tests for both sulfur and iodine. The iodine was determined both by titration, with a standard silver nitrate solution, and by weighing the precipitated silver iodid :

	Per cent.
Iodin found.....	51.392
Necessary for the formula,	
$\text{CH}_2(\text{CH}_3)_2\text{SI}$	
$\begin{array}{c} \text{CH} \\ \text{CH}_2 \end{array} > \text{O}$	51.430

The crystals decompose without melting between 195° to 200°.

The small amount of material prevented farther experiments.

The compounds most closely related to epithiocyanhydrin are the thiocyanacetone and thiocyanpropyl aldehyde. It resembles both in physical properties and in its unstable character.

The thiocyanacetone was reported by Tscherniac in 1883.¹ It is an oil of very disagreeable odor and easily decomposed by heat.

¹Tscherniac : Ber. d. chem. Ges , 16, 349.

The β -thiocyanpropyl aldehyde was prepared by Chautard.¹ It is a liquid of fetid odor, is decomposed by heat, and is easily resinified by acids and alkalies.

Action of Potassium Thiocyanate on Chloranil.

Chloranil or tetrachlorquinone reacts readily with potassium thiocyanate but the resulting compound does not contain the thiocyan group. The chief product is a light brown powder, insoluble in the organic solvents. In ammonia it dissolves, forming a nearly black solution. By nitric acid it is oxidized to sulfuric and oxalic acids. It seems probable that some secondary condensation occurs like that in the case of the monochlorhydrin.

The investigation was not carried farther.

Conclusion.

The results of the experiments may be summarized as follows: The monochlorhydrin, the α,γ -dichlorhydrin, and the acetodichlorhydrin, form corresponding thiocyanates which are very unstable and immediately change to a complex secondary compound.

The α,β -dibromhydrin and its acetic ester form the dithiocyanates which are somewhat more stable and can be separated and purified. Treated with tin and hydrochloric acid they give double chlorids of tin and iminomethanepropylalcohol disulfid.

The epichlorhydrin forms the epithiocyanhydrin readily. It is a liquid of garlic odor insoluble in water but soluble in alcohol and ether. It cannot be distilled. With dry hydrosulfuric acid it forms epihydrin sulfid rather than a dithiocarbamic ester. With methyl iodid it forms epihydrindimethylsulfur iodid.

Chloranil does not give corresponding thiocyanates but complex secondary condensation-products.

SUPPLEMENT.

The action of potassium thiocyanate on a few other haloid ethers was studied with the results given below:

¹ Chautard: Ann. chim. phys., [6] 16, 197.

Action of Potassium Thiocyanate on Tetrabromacetylene.

An attempt was made to prepare tetrathiocyanacetylene from tetrabromacetylene with the expectation of preparing acetylene tetrasulfonic acid from it, by oxidation. At the temperature of the water-bath a mixture of tetrabromacetylene and potassium thiocyanate, containing one molecule of the former to four of the latter, does not change except as the long boiling gradually decomposes the tetrabromacetylene.

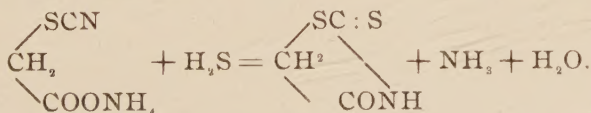
In sealed tubes at temperatures below 130° the separation of potassium bromid is very slow. The contents of the tube blacken and nothing corresponding to a thiocyanate can be separated. At higher temperatures the bromid separates more rapidly. At 160° – 165° the separation is almost theoretical in a few hours. There was much decomposition in the tube and great pressure was developed. Nothing satisfactory was obtained. Apparently the high temperature necessary to produce the reaction is sufficient for the decomposition of the compounds produced.

Action of Potassium Thiocyanate on Iodoform.

The behavior of a mixture of iodoform and potassium thiocyanate is similar to that of tetrabromacetylene and the thiocyanate. The iodine cannot be displaced at temperatures below 100° . At high temperatures there is much general decomposition, and potassium iodide is the only compound that can be separated.

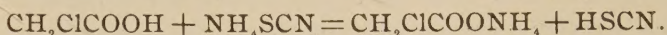
Action of Potassium Thiocyanate on Dibromsuccinic Acid.

Nencki,¹ by boiling a water solution of monochloroacetic acid with ammonium thiocyanate (six molecules of the latter to one of the former), secured rhodanic acid, which is a condensation product of ammonium thiocyanacetate.



¹ J. prakt. Chem., [2] 16, 1.

The hydrosulfuric acid is formed by the decomposition of the thiocyanic acid set free by the action of monochloracetic acid on the ammonium thiocyanate.



Dibromsuccinic acid was heated with ammonium thiocyanate in aqueous solution with the expectation that a reaction similar to that of Nencki's would result. The reaction however seems to end with the formation of the ammonium dibromsuccinate, and the decomposition of the resulting thiocyanic acid.

Nitrils and Sulfur.

The inorganic thiocyanates, when heated in the presence of sulfur, are changed to the thiocyanates. Among the organic cyanids or nitrils however this change does not take place.

Propionic nitril and sulfur were heated in a sealed tube to various temperatures, but even at a temperature of 225° there was no thiocyanate formed, or appreciable change in the amount of free sulfur.

I wish to acknowledge my appreciation of the assistance that has been so kindly furnished by Prof. Marston T. Bogert during this investigation and to here express to him my gratitude for the same.

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